

High Temperature VARTM with LaRC Polyimides¹

Roberto J. Cano
Brian W. Grimsley
Brian J. Jensen
NASA Langley Research Center
Hampton, Virginia 23681

Charles. B. Kellen
Old Dominion University
Norfolk, Virginia 23508

ABSTRACT

Recent work at NASA Langley Research Center (LaRC) has concentrated on developing new polyimide resin systems for advanced aerospace applications that can be processed without the use of an autoclave. Polyimide composites are very attractive for applications that require a high strength to weight ratio and thermal stability. Vacuum assisted resin transfer molding (VARTM) has shown potential to reduce the manufacturing cost of composite structures. In VARTM, the fibrous preform is infiltrated on a rigid tool surface contained beneath a flexible vacuum bag. Both resin injection and fiber compaction are achieved under pressures of 101.3 KPa or less. Recent studies have demonstrated the feasibility of the VARTM process for fabrication of void free structures utilizing epoxy resin systems with fiber volume fractions approaching 60%. In this work, the VARTM process has been extended to the fabrication of composite panels from polyimide systems developed at the Langley Research Center. This work has focused on processing LARC[®] PETI-8 (Langley Research Center Phenylethynyl Terminated Imide- 8), an aromatic polyimide based on 3,3',4,4'-biphenyltetracarboxylic dianhydride, a 50:50 molar ratio of 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy)benzene, with 4-phenylethynylphthalic anhydride as the endcapping agent. Various molecular weight versions were investigated to determine their feasibility of being processed by VARTM at elevated temperatures. An injection temperature of approximately 280°C was required to achieve the necessary viscosity (<5 Poise) for flow at VARTM pressures. Laminate quality and initial mechanical properties are presented for LARC[®] PETI-8 and 6k IM7 uniweave fabric.

KEY WORDS: VARTM, Polyimides, Composites

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1. INTRODUCTION

Polyimides are attractive because of their excellent thermo-oxidative stability and high mechanical properties [1, 2]. In recent years, improvements in processability have made this class of material adaptable to various composite fabrication processes. In turn, applications for polyimides have increased in both the aerospace and electronics industries.

Over the last few decades, the NASA Langley Research Center (LARC) has developed several polyimides that can be melt processed into various useful forms such as coatings, adhesives, composite matrix resins and films. These polyimides are prepared from various aromatic diamines and dianhydrides in several different solvents. Phthalic anhydride has been used as an endcapping agent to control the molecular weight of these thermoplastic polyimides and, in turn, to make them easier to process in the molten form. LARC researchers have also utilized phenylethynylphthalic anhydride as a reactive endcapper on a polyimide backbone to further enhance the properties of polyimides [3-10].

As part of the Next Generation Launch Technology (NGLT) program, work continued to develop structural adhesives and composites for aerospace applications. The NGLT program focused on developing technologies for future reusable launch vehicles with the capability of cost effectively delivering cargo to space. Therefore, lightweight structures are a requirement. These structures include very large cryogenic liquid oxygen (LOX) and liquid hydrogen (LH2) tanks with use temperatures as low as -253°C (-423°F) with hydrogen permeation resistance or -153°C (-297°F) with LOX compatibility. Also required is lightweight, thermal protection system (TPS) support structure that can operate at high temperatures allowing reduced amounts of TPS, thereby saving weight. Since many of the proposed structures are very large, processes that are not size limiting (such as autoclave processing) are desirable if not required. Therefore, development of a non-autoclave processable adhesive and composite was undertaken such that large structures could be produced and efficiently assembled with a limited amount of joints.

As part of a previous program (High Speed Research Program), phenylethynyl terminated imides were developed with an excellent combination of adhesive and composite properties. One material, designated LARC-PETI-5, was selected by the program and developed more extensively as an adhesive and composite matrix resin [6, 7, 11]. While the mechanical and thermal properties are excellent, LARC-PETI-5 requires autoclave processing at 0.5-0.7 MPa (75-100 Psi) external pressure. Because of their success, PETI type materials were again studied to address the NGLT program non-autoclave processing requirements. After numerous compositions were evaluated, a material designated LARC-PETI-8 was selected for additional development. LARC-PETI-8 produces excellent tensile shear strengths and flatwise tensile strengths when processed with vacuum bag pressure only [12], eliminating the need for costly autoclave processing.

Vacuum assisted resin transfer molding (VARTM) is a unique composite manufacturing process where both resin injection and fiber compaction are achieved under pressures of 101.3 KPa or less. Recent developments in the VARTM process have produced composite parts with fiber volumes approaching 60% [13]. This, combined with the comparably low production costs and

low volatile emissions associated with the process, makes VARTM an attractive processing technique for the manufacture of large-scale composite aerospace structures.

The VARTM process was developed as a variation of resin transfer molding (RTM) over ten years ago for application in commercial and military, ground-based and marine composite structures [14,15]. The upper tool of the matched metal mold used in RTM is replaced in the VARTM process by a formable vacuum bag material. Both transfer of the matrix resin and compaction of the part are achieved using atmospheric pressure alone. Flow of the resin into the part is improved through the use of a resin distribution medium [16,17]. The highly-permeable medium induces resin flow through the thickness of the part, which reduces filling times.

PETI oligomers for high temperature RTM, vacuum assisted RTM (VARTM) and resin infusion (RI) have been under investigation since the late 1990s. To demonstrate the versatility and processing robustness of these resins, complex composite parts such as I-beams, F-frames and skin stringer panels have been fabricated using RTM and RI. VARTM has provided flat laminates with mechanical properties equivalent to laminates fabricated by RTM. Recent efforts have focused on increasing the use temperature by modifying the chemistry to effect as high a T_g as possible without causing an increase in melt viscosity [18,19,20,21]. Composite processing by VARTM and properties of IM7/LARCTM PETI-8 are reported in this paper.

2. EXPERIMENTAL[□]

2.1 LARCTM PETI-8 Polyimide Powder LARCTM PETI-8 polyimide powder was supplied by Imitec, Inc. (Schenectady, NY) with theoretical number average molecular weights of ~ 1,250, ~1,125, and ~1,000 g/mol. Poly(amide acid) was synthesized by mixing 3,3',4,4'-biphenyltetracarboxylic dianhydride, and a 50:50 molar ratio of 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy) benzene with 4-phenylethynylphthalic anhydride as the endcapping agent in NMP. The poly(amide acid) was then fully imidized into a powder and dried. The synthetic scheme for preparing compositions of LARCTM PETI-8 polyimide is similar to that of LARCTM PETI-5 (5,000 g/mole theoretical number average molecular weight) as reported in literature [7] and is shown in Figure 1. The molar amount of dianhydride was limited compared to the molar amount of diamine with an appropriate amount of PEPA endcapper to prepare the different molecular weight PETI-8 materials used in this study. Adhesive properties and processing characteristics of PETI-8 are available in reference 12. Composite preparation from IM7/ PETI-8 poly(amide acid) unidirectional tape and their properties are available in reference 22.

[□] Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

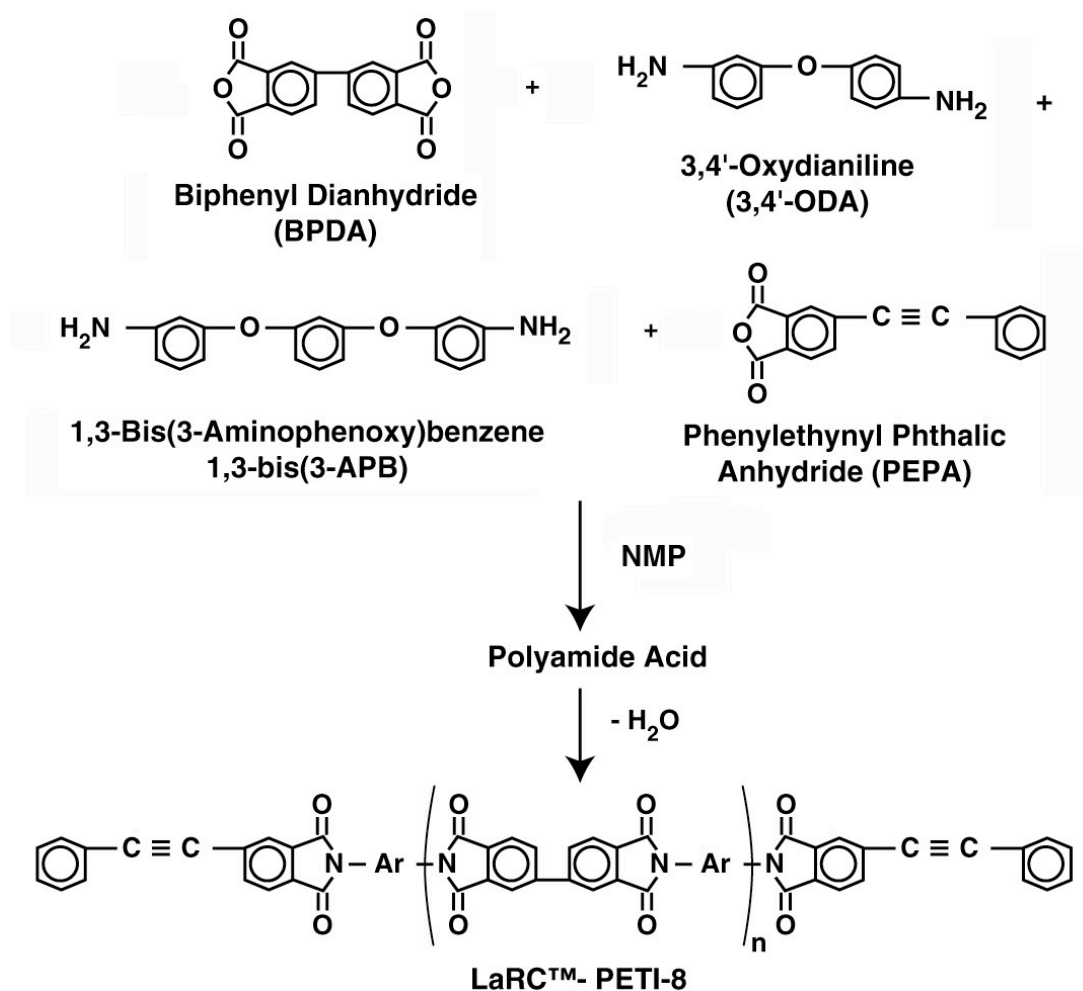


Figure 1. Synthesis of LaRC- PETI-8.

2.2 Fiber Preform IM7 6K Sticky String Stabilized Uniweave with a nominal fiber areal weight of 164 g/m² was supplied by Textile Products Incorporated (Anaheim, CA).

2.3 Thermogravimetric Analysis (TGA) The residual solvent content/ mass loss in the matrix resin was measured using a NETZSCH STA409CD thermogravimetric analyzer (TGA) coupled with a quadrupole mass spectrometer at a heat-up rate of 10°C/min in flowing helium.

2.4 Differential Scanning Calorimetry (DSC) A Shimadzu DSC-50 calorimeter was used to study glass transition temperature (T_g) of the imidized resins at a heating rate of 20°C/min. The T_g was taken at the inflection point of the endotherm.

2.5 Gel Permeation Chromatography-Differential Viscometry (GPC-DV) Number average (M_n), and weight average (M_w) molecular weights and intrinsic viscosities (IV_n) of each powder was determined with a Waters 150-C gel permeation chromatograph coupled with a Viscotech 150R viscometer.

2.6 Melt Rheology Dynamic rheological measurements were conducted using a parallel-plate fixture on a Rheometrics ARES rheometer. The lower plate was oscillated at a fixed strain of 10% and a fixed angular frequency of 10 rad/sec while the upper plate was attached to a transducer which recorded the resultant torque. The as-received powders were press molded at room temperature (RT) into 2.54 cm diameter and ~ 1.5 mm thick disks. Each specimen was then loaded and heated from RT to 280°C at 2°C/min and held for various times. Storage (G') and loss (G'') moduli were measured as a function of time (t) during the temperature ramp. These moduli were then converted to the complex viscosity $\eta^*(t)$. The imide softening point and the minimum viscosity were identified from the measurements.

2.7 High Temperature VARTM The VARTM set-up utilized in this work is shown in Figure 2. A half-inch thick steel plate was utilized as a tool. Three holes were drilled and tapped into the plate to provide one resin inlet and two vacuum outlets. Aluminum screen material was utilized as the flow medium. Polyimide bagging material and high temperature sealant was used to seal both an inner bag that contained the fiber preform, flow media and breather material and an outer bag that provides redundancy should a leak occur in the inner bag after infiltration. The tool was placed in an air circulating oven and heated to 280°C. The resin pot, which had been heated in a separate oven to melt the resin powder and cooled to create a seal for the inlet tube, was not placed in the oven until the tool had reached temperature to minimize time-at-temperature affects to the resin. The resin pot was then plumbed to the tool and allowed to heat in the same oven. Vacuum was pulled on both the inner bag and the resin pot as the resin was heated in order to degas the resin and remove air from the perform. Infiltration began when the resin reached 280°C corresponding to its minimum viscosity by releasing the vacuum on the resin pot and allowing atmospheric pressure to push the resin into the preform. Once the panel was filled, vacuum was pulled on the second bag and the entire system was then cured at 371°C for one hour.

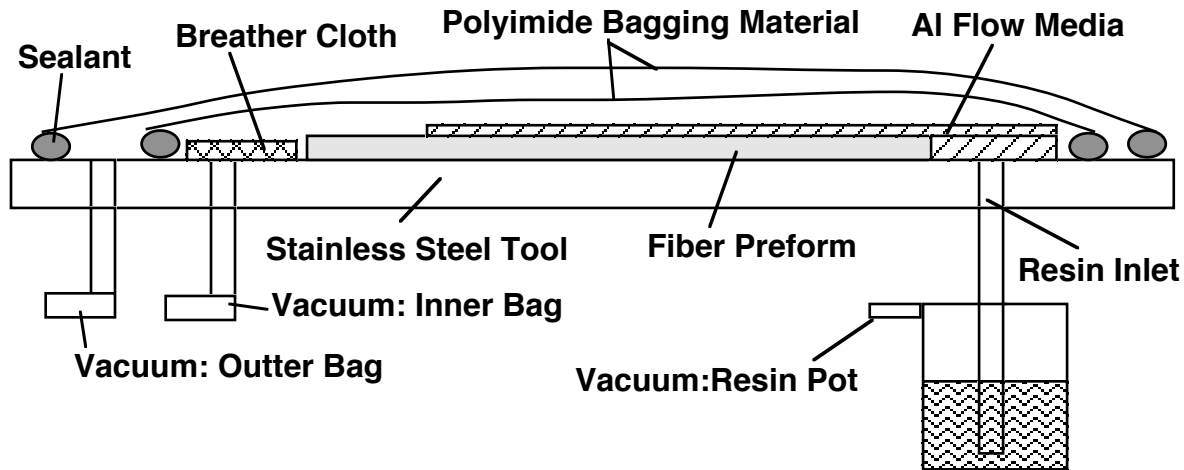


Figure 2. Schematic of High Temperature VARTM Set-up.

2.8 Composite Mechanical Properties Composite mechanical properties including short beam shear strength (SBS) (ASTM-D2344), and flexural strength and modulus (ASTM-D790) were measured at RT and elevated temperatures. Test equipment and procedures were the same as those previously reported [3].

3. RESULTS

The as-received PETI-8 powders were evaluated to determine their molecular weights by GPC-DV. The GPC-DV measurements are presented in Table 1. For all three materials, the experimentally determined number average molecular weights were higher than the theoretical values. Experimental error associated with separation efficiencies in the GPC technique at these low molecular weights may be responsible for the differences. However, the experimental results did indicate a consistent difference of approximately 200 g/mol between the powders compared to the theoretical difference of 125 g/mole. The glass transition temperature data from DSC of the three versions of the PETI-8 powder as well as their mass loss from TGA are presented in Table 2. As expected, the Tg of the material decreased with an increase in molecular weight. As molecular weight increases, the resultant crosslink density decreases which will result in a lowering of the Tg. The 1000 g/mol version had a Tg of over 300°C. The viscosity data generated from parallel plate rheology are presented in Table 3. Since the phenylethynyl groups are known to begin reacting above 280°C, a processing temperature of 280°C was chosen to provide the lowest viscosity with the largest processing window. Typically, a viscosity of 5 poise or less is required for most VARTM processes. Therefore, a threshold of 5 poise was chosen for determining process window times. As shown in Table 3, the PETI-8/1250 did exhibit a melt viscosity of 5 poise, but it did not maintain that viscosity for any appreciable amount of time. The PETI-8/1125 reached a minimum viscosity of 3.5 poise at 280°C with a process window of about 78 minutes below 5 poise. The PETI-8/1000 demonstrated a minimum viscosity of 1.3 poise at 280°C and a process window of about 200 minutes below 5 poise. The viscosity data for the PETI-8/1000 is plotted in Figure 3. Since the PETI-8/1000 provided the lowest minimum viscosity, the largest processing window, and the highest Tg, it was selected for further evaluation in this work.

Table 1. GPC-DV Measurements for PETI-8.

Material	Theoretical M_n, g/mole	Experimental M_n, g/mole	Experimental M_w, g/mole	Experimental IV_n, dL/g
PETI-8/1000	1000	1710	1930	0.0386
PETI-8/1125	1125	1900	2150	0.0417
PETI-8/1250	1250	2100	2470	0.0475

Table 2. Cured Tg after 1 hour at 371°C from DSC and mass loss from TGA.

Material	Tg, °C	Mass Loss, %
PETI-8/1000	301	2.78
PETI-8/1125	293	2.24
PETI-8/1250	275	1.42

Table 3. Processing Windows of LaRC PETI-8.

Material	Min. Viscosity @ 280°C, poise	Time @ <5 poise & 280°C, min.
PETI-8/1000	1.3	200
PETI-8/1125	3.5	78
PETI-8/ 1250	5.0	0

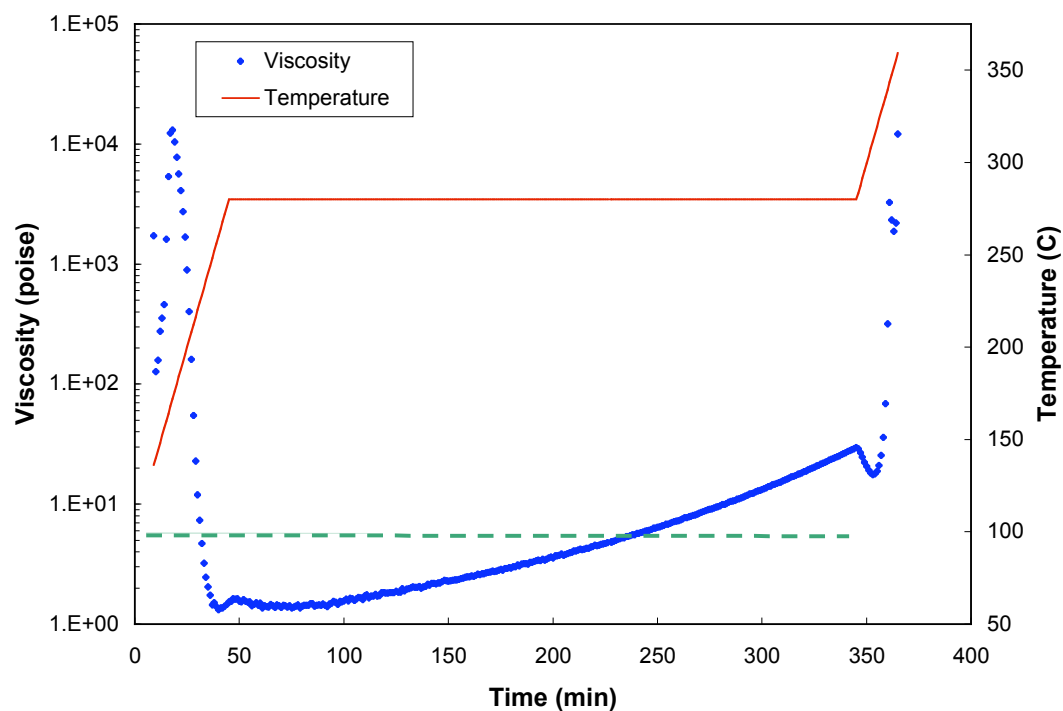


Figure 3. Rheology profile of PETI-8, 1000 g/mol powder.

Composite panels from the PETI-8/1000 powder and IM7 6k uniweave were fabricated by VARTM and evaluated by acid digestion and optical microscopy. The volume fractions of three panels are presented in Table 4. As shown in the table, fiber volume fractions ranged from 51 to 58 percent. However, void contents were high, ranging from 7.5 to 9.2 percent by acid digestion and ranging from 4.2 to 10.6 percent by optical microscopy. Although not optimized, the results indicate that composite panels can be fabricated by VARTM with the PETI-8 material. Figure 4 shows photomicrographs of a PETI-8/1000 VARTM panel. As shown in the left photo, voids are clearly visible in the panel. However, magnification of the panel does indicate that the void-free areas are well wet-out. It is anticipated that with refinement of the processing parameters and tooling improvements higher quality panels can be achieved. Panels were fabricated from a uniweave material that has been determined to have a much lower through-the-thickness (TTT) permeability than other textile performs that have been evaluated at LaRC, such as multiaxial warp knit (MAWK) fabric and biaxial satin weaves. The through-the-thickness permeability of a quasi isotropic perform made from the uniweave utilized in this work was determined to be approximately $2.5 \times 10^{-14} \text{ m}^2$ which is significantly lower than the MAWK fabric permeability of $7.5 \times 10^{-13} \text{ m}^2$ and the biaxial fabric TTT permeability of $1.2 \times 10^{-12} \text{ m}^2$. This low permeability hinders the ability of the resin to properly wet-out the fabric. Another potential issue is the removal of the sizing from the preform, which can adversely affect permeability and make infiltration even more difficult. TGA measurements of the fiber perform itself indicate a mass loss of about 0.4% at the 280°C infiltration temperature and an additional 1.3% mass loss during the 371°C cure. To date permeability measurements on unsized fabric have not been performed at LaRC. Since the perform sizing was not burned off prior to infiltration, these by-products may result in void formation. The initial mass loss may effect the preform permeability and will require further investigation. More care will be required in removing the sizing of the perform prior to injection. TGA measurements (Table 2) of the PETI-8/1000 as received powder indicate a 2.78 % mass loss from the resin at 371°C, which could also be another source of void formation. Since VARTM utilizes such low compaction pressures, void formation is difficult to overcome with processing pressure. Therefore, identifying the source of this mass loss and eliminating it should result in improved (void-free) laminates

Table 4. Volume fractions of PETI-8, 1000 g/mol VARTM process panels.

Panel	Lay-up	Fiber Vol., %	Void Vol., %	Optical Void Vol., %
061804	[0]₁₅	56	8.9	4.6
061604	[0]₁₀	58	7.5	10.6
051204	[0]₂₀	51	9.2	4.2

Preliminary mechanical test results from the PETI-8 composite panels fabricated by VARTM are presented in Table 5. Panels were tested to determine their SBS strengths at RT and 288°C. At room temperature, the IM7 uniweave/ PETI-8 panels resulted in SBS values of ~70-75 MPa (10-11 ksi) for two different panels. At 288°C, Panel 061804 retained 46% of its RT value. Although the percentage of strength retention was not as high as those reported in the literature [21] for a similar VARTM processable polyimide system, LaRC PETI-298, the absolute values of the PETI-8/1000 SBS strengths were twice as high at RT and 35% higher at 288°C. However,

it should be noted that a different preform type and fiber was utilized in that work. Flexural strengths of approximately 110 ksi at RT were determined for the PETI-8 material processed via VARTM.

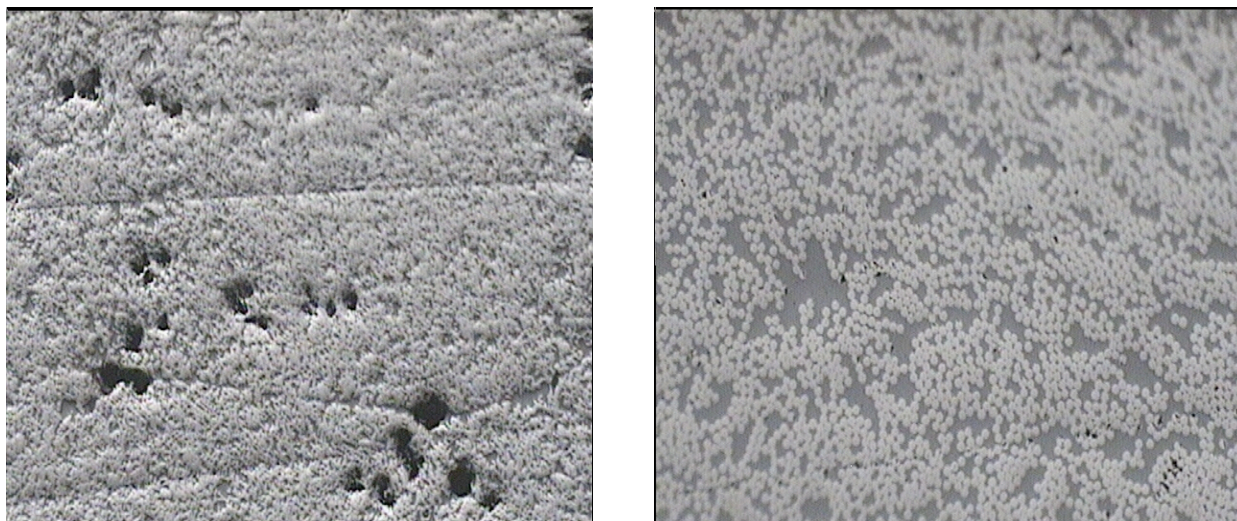


Figure 4. Photomicrographs of PETI-8 VARTM Panels. (Left 5X, Right: 20X)

Table 5. Mechanical test results of PET-8/1000/ IM7 6K uniweave VARTM Panels.

Panel	SBS @ RT, MPa	SBS* @ 288°C, MPa	0° Flex @ RT, MPa
061804	75.1 ± 2.1	34.5 ± 2.8	n/a
051204	66.9 ± 4.8	n/a	n/a
061604	n/a	n/a	757 ± 20

*** ASTM D2344: Failure criteria based on crosshead displacement of specimen thickness**

4. SUMMARY

LaRC PETI-8 imide powder was demonstrated to have the required characteristics to be utilized in a high temperature VARTM process. The three theoretical number average molecular weight versions, ~1000, ~1125, and ~1250 g/mole all had minimum viscosities of 5 poise or less at 280°C. The 1000 g/mol version provided a 200-minute processing window during which the viscosity remains below 5 poise at 280°C. Since this version of the material provided a relatively large processing window and a Tg of over 300°C, it was utilized to successfully fabricate composite panels by VARTM. Fiber volume fractions as high as 58% percent were achieved. However, a void content of 7.5 percent was determined for this panel. Initial mechanical properties resulted in a SBS strength of 75.1 MPa (10.9 ksi) at RT with 46% retention of strength at 288°C. Although these are only preliminary properties and initial high temperature VARTM trials, PETI-8 does appear to be a candidate for the fabrication of composites by high temperature VARTM processes. Further work to improve the VARTM process at elevated temperature as well as further understanding of the permeability of unsized performs should result in higher quality panels and improved mechanical properties.

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